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PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Preparation of Polyethylene/Fumarate Diester Graft Copolymers

We, ALLIED CHEMICAL CORPORATION, a Corporation organized and existing under the laws of the State of New York, United States of America, of 61 Broadway, New York 6, New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

THIS INVENTION relates to a process for the preparation of a high density polyethylene/fumarate diester graft copolymer employing a hydroperoxide initiator.

High density polyethylene is a relatively inexpensive and very useful polymer and can be made, for example, by processes described in U.S. Patents Nos. 2,825,721 and 2,949,447. However, it suffers from certain inherent disadvantages which render it unsuitable for for some applications. For example, the homopolymer is quite brittle and substantially inextensible. Similarly, both the high homopolymer and known copolymers are susceptible to stress cracking and somewhat deficient in impact resistance. Obviously, an inexpensive high density ethylene polymer which does not have the aforementioned undesirable properties is desirable.

The process according to the invention for producing a graft copolymer comprises mixing a composition comprising (A) 70 to 99.5%, preferably 80—95%, by weight of the ethylene polymer having a density of at least 0.940 g/cc determined as herein defined and containing 90—100% by weight of ethylene in the polymer chain and (B) 0.5 to 30% preferably 5 to 20% by weight of a fumaric acid diester, at a temperature above the melting point of the polymer, in the presence of at least 0.02%, based on the weight of the composition, of a hydroperoxide having a half life of at least one minute at 145° C.

The new graft copolymers possess better flexibility, extensibility, and impact resistance than high density polyethylene homopolymers.

In a preferred embodiment of the invention, the ethylene polymer has a density of from 0.942 to 0.965 g/cc determined as herein defined and contains at least 98% by weight of ethylene in the polymer chain. Preferably also each esterifying residue of the fumaric acid diester is an alkyl hydrocarbon or chlorinated hydrocarbon radical containing from 1 to 18 carbon atoms. While the amount of the fumaric acid diester actually incorporated into the graft copolymer may vary somewhat, it is preferred that it be present in the polymer in amount from 0.5 to 12% by weight.

The terminology "graft copolymer" is employed to signify that the monomeric material (fumaric acid diester) reacts with the residual unsaturated groups in the ethylene polymer to couple or form branches which extend the polymer chains rather than cross-link them with the formation of insoluble "gel".

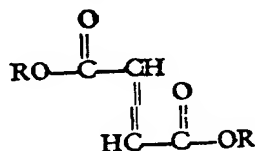
The expression "an ethylene polymer having a density of at least 0.940 and containing at least 90% by weight of ethylene in the polymer chain" signifies the conventional low pressure polyethylenes as described, for example, in U.S. Patents No. 2,949,447 and 2,825,721. The polymer may be the homopolymer or a copolymer obtained by reacting ethylene with a comonomer such as propylene; butene - 1; butene - 2; 3 - methyl butene - 1; pentene - 1; hexene - 1; 1,3 - butadiene, or another suitable comonomer as described in the aforementioned patents, as well as mixtures of such comonomers.

The linkage of the fumaric acid diester to the ethylene polymer takes place primarily on the terminal vinyl groups of the polymer chain. Unlike the low pressure polyethylenes

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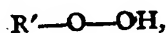
employed in the present invention, high pressure polyethylenes, which are amorphous rather than crystalline, do not contain a significant proportion of terminal vinyl groups and are not suitable for use in the present invention. In order to graft fumaric acid diesters onto high pressure polyethylene there must be used longer reaction times and larger excesses of the diesters than in the present invention, and the product obtained is of a different character, having a random distribution of the diester branches rather than linkages primarily on the terminal groups.

The fumaric acid diesters suitable for use in the present invention have the formula



wherein R is an organic radical, preferably a hydrocarbon or chlorinated hydrocarbon radical of 1 to 18 carbon atoms, e.g. alkyl of 1 to 18 carbon atoms, aryl of 6 to 10 carbon atoms, alkyl substituted aryl of 7 to 18 carbon atoms, alicyclic of 3 to 7 carbon atoms, or a chlorine substituted derivative of any of the above. Among the suitable fumarate diesters are: dimethyl fumarate; dipropyl fumarate; diisobutyl fumarate; dibutyl fumarate; dipentyl fumarate; dicyclopentyl fumarate; dihexyl fumarate; dicyclohexyl fumarate; dioctyl fumarate; didodecyl fumarate; di(2-phenylethyl) fumarate; di(2-ethylhexyl) fumarate; di(tetrahydrofurfuryl) fumarate; *p*-chlorophenyl methyl fumarate; methyl ethyl fumarate; ethyl butyl fumarate; propyl cyclohexyl fumarate; and phenyl ethyl fumarate. The fumaric acid diester links to the polyethylene through the olefinic unsaturation of the diester.

Any of the known hydroperoxides which have a half life of at least one minute at 145°C. may be employed. Such hydroperoxides have the general formula



wherein R' is an organic radical. Among the suitable hydroperoxides are *t*-butyl hydroperoxide, *p*-methane hydroperoxide, pinane hydroperoxide, and cumene hydroperoxide, but others are known.

It is essential that the hydroperoxide be present as initiator. If it is not employed, the reaction rate is not only uneconomically slow, but frequently the required minimum amount of fumarate diester cannot be grafted into the polymer even after a prolonged reaction time. The weight of hydroperoxide is preferably 0.1 to 5% by weight of the molten composition.

In carrying out the process of the invention, the components of the composition are merely mixed and heated to a temperature above the melting point of the ethylene polymer. Preferably the molten composition is mixed in the presence of the hydroperoxide for a period of 3 seconds to 20 minutes. The elevated temperature causes rapid decomposition of the hydroperoxide, with formation of the graft copolymer. Obviously, the more homogeneous the mixture prior to heating, the less mixing of the molten composition will be required. However, in order to obtain a desirable conversion, it has been found that some form of mixing is highly desirable even when a uniform mixture of all of the components of the composition is formed prior to heating. In general, the composition should be heated to a temperature above about 130°C. and it is preferred to use temperatures ranging from 270 to 320°C. Temperatures substantially above about 325°C. are generally to be avoided, since they may cause substantial decomposition of the polymers. However, if the decomposition products are not undesirable in the product, higher temperatures may be employed. The reaction time required is quite short, e.g. from a few seconds to about twenty minutes.

A convenient method of performing the reaction is to premix the ingredients and then extrude the composition through a heated extruder but other mixing means, such as a Banbury mixer, or a roll mill, may also be employed. In order to prevent undue increase in molecular weight, and the possibility of some cross-linking at elevated temperatures, it is desirable to carry out the reaction in a closed reaction vessel. A conventional extruder accomplishes this result without the use of auxiliary equipment and for this reason provides a particularly desirable reactor.

The following Examples illustrate the invention; parts and percentages are by weight. Densities are given in grams per cubic centimeter at 23°C. as measured in a density gradient column such as that described in "Journal of Polymer Science", vol 21, p, 144, 1956.

The "melt index" (designated I_2) is reported in decigrams per minute and is determined by the standard ASTM-D-1238-59T test, except that when this method gives a value of 0.0, a modified method in which the melt index is designated I_{21} is employed which utilizes a 21,600 gram weight instead of a 2,160 gram weight, all other conditions remaining the same. This modification merely gives a better indication of very low indices.

The percent elongation, the tensile strength at yield, and the ultimate tensile strength are measured by the standard ASTM-D-638-60T test.

The "high density" ethylene polymers em-

ployed in the Examples are prepared by the process of U.S. Patent 2,949,447 or 2,825,721 using a pressure of about 31.5 kg/cm², a temperature (in the former case) of 96°—5—99°C., a reaction time of about 2 hours and as catalyst chromium oxide supported on silica/alumina. When employing the procedure of U.S. Patent 2,825,721, the polymerization temperature is as indicated in the Examples of the above U.S. specification.

The melting point of the polymer is determined by the conventional procedure employing a polarizing microscope. The amount of the fumarate diester actually incorporated into the polymer is determined on a weight-percentage basis by infrared analysis (Perkin-Elmer Model 21 Spectrometer).

The extruders used were of the tubular

Pressure	Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Die	RPM
77 kg/cm ²	197°C.	221°C	238°C.	277°C.	266°C.	321°C.	150°C.	25

The graft copolymer obtained was purified by recrystallization from xylene and then methanol. The product had a density of 0.964, a melting point of 118°C, and a melt index I₂ of 0.31, and contained 8.4% of diethyl fumarate. Test specimens were prepared by compression moulding and found to have a tensile strength at yield of 139.3 kg/cm² and an elongation at break of 1120%.

EXAMPLE 2

To 94.9 parts of the same ethylene - butne - 1 copolymer were added 5 parts of diethyl fumarate and 0.1 part of butyl hydroperoxide. The mixture was placed in a "Sterling" ("Sterling" is a Registered Trade Mark) one inch extruder having a length/diameter ratio of 24:1 and the following heat profile: Zone 1=204°C.; Zone 2=315°C.; Zone 3=204°C.; and die =204°C.

The graft copolymer obtained was purified by recrystallization from xylene and then methanol, giving a product having a melt index I₂₁ of 10.0, a melting point of 121°C, and a density of .945, and containing 1.9% of diethyl fumarate. Test specimens were prepared by compression moulding and found to have a tensile strength at yield of 188.5 kg/cm² and an elongation at break of 600%.

EXAMPLE 3

The procedure of Example 2 was repeated, using 89.9 parts of the ethylene - butene - 1 copolymer, 10 parts of diethyl fumarate, and 0.1 parts of t - butyl hydroperoxide. The graft copolymer obtained had a melt index I₂ of 0.69, a melting point of 120°C. and a density of .948, and contained 3.2% of diethyl fumarate. Test specimens of the polymer were found to have an average ultimate tensile strength at yield of 163.4 kg/cm² and an elongation at break of 665%.

type with a screw feed; the heating chambers contained a plurality of zones maintained at different temperatures by means of an electric heating element surrounding each zone. The temperature profile is given from Zone 1 (feed end of the machine) to the zone immediately adjacent to the extrusion die.

EXAMPLE 1

To 466 grams of a copolymer of high density ethylene and butene - 1, of density .943 and melt index I₂₁, were added 114 grams of diethyl fumarate and 7.05 grams of t - butyl hydroperoxide. The mixture was placed in a "Killion" one inch (2.54 cm) extruder with a nylon type screw of length/diameter ratio 16:1 and compression ratio 3:1. The following conditions were used:

EXAMPLE 4

The procedure of Example 2 was repeated, using 84.9 parts of the copolymer, 15 parts of diethyl fumarate, and 0.1 part of t - butyl hydroperoxide. The graft copolymer obtained had a melt index I₂ of 2.42, a melting point of 118.5°C. and a density of .952 and contained 4.5% of diethyl fumarate. Test specimens of the polymer were found to have an average ultimate tensile strength at yield of 182.6 kg/cm² and an elongation at break of 750%.

EXAMPLE 5

The procedure of Example 2 was repeated, using 79.9 parts of the copolymer, 20 parts of diethyl fumarate, and 0.1 part of t-butyl hydroperoxide. The graft copolymer obtained had a melt index I₂ of 9.00, a melting point of 118.5°C. and a density of .956, and contained 5.1% of diethyl fumarate. Test specimens of the polymer were found to have an average ultimate tensile strength at yield of 135.8 kg/cm² and an elongation at break of 670%.

EXAMPLE 6

Other graft copolymers are obtained by substituting equal molar amounts of the following fumaric acid diesters for the diethyl fumarate employed in Examples 1 to 5: dimethyl fumarate; dipropyl fumarate, diisobutyl fumarate; dibutyl fumarate; dipentyl fumarate; dicyclopentyl fumarate; dihexyl fumarate; dicyclohexyl fumarate; dioctyl fumarate; didodecyl fumarate; dibenzyl fumarate; di(2 - phenylethyl) fumarate; di(2 - ethylhexyl) fumarate; di(tetrahydrofurfuryl) fumarate; p - chlorophenyl methyl fumarate; methyl ethyl fumarate; ethyl butyl fumarate; propyl cyclohexyl fumarate and phenyl ethyl fumarate.

EXAMPLE 7

Other graft copolymers are obtained by substituting equal molar amounts of other ethylene polymers for the ethylene - butene-1 copolymer of Examples 1 to 5; in particular graft copolymers having properties similar to the products of Examples 1 to 5 are obtained by the use of high density ethylene homopolymers prepared in accordance with U.S. Patents 2,825,721 and 2,949,447.

The graft copolymers can be fabricated into useful articles by the same procedures as high density homopolymers, e.g. blow moulding, injection moulding, compression moulding, extrusion and rolling.

WHAT WE CLAIM IS:—

1. A process for producing a graft copolymer which comprises mixing a composition comprising (A) 70 to 99.5% by weight of an ethylene polymer having a density of at least 0.940 g/cc determined as hereinbefore defined and containing 90—100% by weight of ethylene in the polymer chain and (B) 0.5 to 30% by weight of a fumaric acid diester, at a temperature above the melting point of the ethylene polymer, in the presence of at least 0.02%, based on the weight of the composition, of a hydroperoxide having a half life of at least one minute at 145°C.
2. A process according to claim 1, wherein the composition comprises 80 to 95% by weight of the ethylene polymer and 5 to 20% by weight of the fumaric acid diester.

3. A process according to claim 1 or 2 wherein the ethylene polymer has a density of 0.942—0.965 g/cc determined as hereinbefore defined and contains 98—100% of ethylene.

4. A process according to any one of the preceding claims, wherein the molten composition is mixed with 0.1 to 5% of the hydroperoxide.

5. A process according to any one of the preceding claims, wherein the composition is heated to a temperature of 270 to 320°C.

6. A process according to any one of the preceding claims, wherein the molten composition is mixed in the presence of the hydroperoxide for a period of 3 seconds to 20 minutes.

7. A process as claimed in any one of the preceding claims, wherein the esterifying residues in the fumaric acid diester are alkyl groups of 1 to 18 carbon atoms or chlorinated derivatives thereof.

8. A process for producing a graft copolymer according to claim 1 substantially as hereinbefore described.

9. Graft copolymers obtained by a process claimed in any one of claims 1—8.

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